Cyclobutyl β-Naphthalenesulfonate Solvolysis.   Solvolytic Behavior Study

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The solvolysis rates of cyclobutyl β-naphthalenesulfonate (4-ONas) have been determined in a series of solvents of varying ionizing strength. The correlation of 4-ONas solvolysis rates with those of 2-adamantyl tosylate and pinacoyl brosylate reveals that 4-ONas suffers solvolysis with little nucleophilic assistance by solvent but with considerable anchimeric assistance. The product distributions of 4-ONas in a wide spectrum of solvents corroborates the absence of significant nucleophilic participation by solvent.

Considerable evidence[1,2] has been presented to support the contention that the unusual solvolytic reactivity of cyclopropylcarbinyl derivatives in a wide spectrum of solvents is due to anchimerically assisted ionization (k_Δ)[3,4] and not due to solvent nucleophilic participation (k_s).[3,4]

The relative importance of anchimeric (k_Δ) and solvent (k_s) assistance upon the overall solvolysis rate (k_t) of cyclobutyl derivatives (in the same spectrum of solvents) is less well defined.[5,6] In part, this is due to the lack of a suitable model for evaluating the unassisted ionization rates (k_c)[3,4] of secondary substrates.

Recently, two such models have been proposed, 2-adamantyl tosylate[4] and 3,3-dimethyl-2-butyl (pinacoyl) brosylate.[7] The former is described[4] as a new standard for k_c-type behavior without mention of ion-pair return. The latter is proposed[7] as a new standard for k_c-type behavior unaccompanied by ion-pair return.

This paper reports the results of an investigation where the solvolytic behavior of cyclobutyl β-naphthalenesulfonate, 4-ONas, was compared with that of 2-adamantyl tosylate and pinacoyl brosylate. The data indicate that cyclobutyl β-naphthalenesulfonate suffers solvolysis in a wide range of solvents with little nucleophilic assistance by solvent but with considerable anchimeric assistance.

The first-order rate constants for solvolysis of cyclobutyl β-naphthalenesulfonate in various solvents are summarized in Table I. The reaction progress was followed by titrating the liberated β-naphthalenesulfonic acid. The solvolysis reaction of 4-ONas in 2,2,2-trifluoroethanol was accompanied by 22% internal return isomerization.[8] The apparent first-order rate constants, k_t, in this solvent were computed on the basis of the acid infinity titer and, therefore, are a sum of the rearrangement and the solvolytic rate processes. The fact that the infinity titers in urea buffered and unbuffered reactions were identical supports an internal return isomerization and not a competing acid-catalyzed isomerization.

The product distribution data listed in Table II reveal a marked similarity in all solvents. This result strongly suggests that the same cationic species reacts with solvent in all the investigated solvolysis reactions. The possibility that the reported product distributions

TABLE I
Solvolysis Rates for Cyclobutyl β-Naphthalenesulfonate

Solvent	Temp, °C	k_1, 10^5 sec^{-1}	Infinity %
HCO$_2$H[a]	15	86 ± 1	100
	20	160 ± 5	100
	25	270 ± 8	100
	25	430 ± 7[b]	100
	30	400 ± 10	100
CF$_3$CH$_2$OH[c]	25	10 ± 0.2[d]	77
	35	25 ± 0.5	78
	44	58 ± 2[d,e]	78
	50	99 ± 0.5	78
EtOH	50	1.36 ± 0.04	100
	50	1.38 ± 0.05[f]	100
	50	1.38 ± 0.03[g]	100

[a] $\Delta H^{\ddagger} = 17.2 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -13 \pm 1$ eu. [b] Sample 0.045 M in HCO$_2$Li and 0.015 M in ester. [c] $\Delta H^{\ddagger} = 16.9 \pm 0.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -20 \pm 1$ eu. [d] Duplicate run. [e] Sample 0.040 M in urea and 0.030 M in ester. [f] Sample 0.010 M in NaN$_3$ and 0.030 M in ester. [g] Sample 0.015 M in NaN$_3$ and 0.030 M in ester.

are the result of subsequent isomerization reactions has been ruled out by previously reported product stability studies.[1,2,9]

It is particularly noteworthy that the amount of unrearranged ethanolysis product is no greater than the amount of unrearranged formolysis product. This observation coupled with the very low degree of nucleophilic participation by azide ion[10] argues in favor of a similar low degree of nucleophilic participation by solvent in the ethanolysis reaction of 4-ONas.

The correlation of the cyclobutyl β-naphthalenesulfonate solvolysis rates with those of (a) neophyl tosylate, (b) 2-adamantyl tosylate, and (c) pincaoyl brosylate (cf. Figure 1) affords considerable insight concerning the relative importance of the k_Δ and k_s pathways in the solvolysis of 4-ONas. For instance, the good linear free-energy correlation between log k for 4-ONas and neophyl tosylate can be interpreted in terms of discrete k_Δ and k_s solvolysis processes[12] and, more importantly, that the k_Δ route is dominant for the solvolysis of 4-ONas in all investigated reactions. This interpretation is true to the extent that log k_t (neophyl tosylate) is a good model for anchimerically assisted solvolyses.[13]

(1) D. D. Roberts, *J. Org. Chem.*, in press.

(2) D. D. Roberts and T. M. Watson, *ibid.*, **35**, 978 (1970).

(3) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

(4) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).

(5) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(6) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(7) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(8) K. L. Servis and J. D. Roberts, *Tetrahedron Lett.*, 1369 (1967).

(9) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

(10) The incorporation of azide ion, *cf.* Table I, produces almost no rate enhancement for the ethanolysis of 4-ONas. This compares with a threefold rate enhancement observed[11] in the solvolysis of isopropyl tosylate under similar concentration conditions in more strongly ionizing 80% aqueous ethanol.

(11) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5729 (1970).

(12) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969).

(13) For leading references, see A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

TABLE II

SOLVOLYSIS PRODUCTS FOR CYCLOBUTYL β-NAPHTHALENESULFONATE

Solvent	Buffer	![OS structure]	▷—CH₂OS	CH₂=CHCH₂CH₂OS
EtOH	C₅H₅N	42	53	5
AcOH	NaOAc	44	52	4
AcOH	NH₂CONH₂	45	51	4
HCO₂H[a]	HCO₂Na	45	45	10

[a] Taken from data of K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).
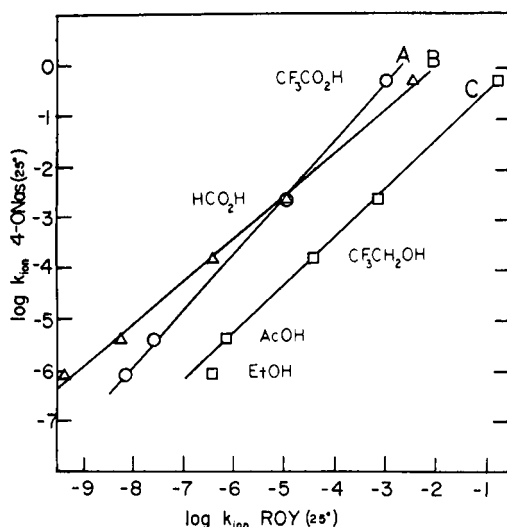

Figure 1.—The linear dependence of log k_{ion} for 4-ONas on log k_{ion} for neophyl tosylate, A; on log k_{ion} for 2-adamantyl tosylate, B; on log k_{ion} for pinacoyl brosylate, C.

It is also seen in Figure 1 that a good linear free-energy correlation exists between log k for 4-ONas and log k_t for 2-adamantyl tosylate, a model for limiting[4] solvolytic behavior. This observation corroborates the interpretation that the k_s pathway plays only a minor role in the solvolysis reactions of 4-ONas.

The correlation between log k for 4-ONas and log k_t for pinacoyl brosylate further reinforces the interpretation that nucleophilic participation by solvent plays a minor role in the solvolysis of 4-ONas. The accelerated ethanolysis rate of pinacoyl brosylate observed in this correlation is also observed in a similar correlation with log k_t for 2-adamantyl tosylate and lends additional support to the contention that the ethanolysis of 4-ONas is accompanied by only a low degree of nucleophilic participation by solvent.

Finally, the large magnitude of the k_A/k_c data recorded in Table III are cited in support of the specula-

TABLE III

ASSISTED/UNASSISTED RATE RATIOS FOR 4-ONAS, 25°

Solvent	$\dfrac{k^{4\text{-}ONas}}{k^{2\text{-}AdOTs}}$	k_A/k_c[a] 4-ONas
CF₃CO₂H	$10^{2.13}$	$10^{5.23}$
HCO₂H	$10^{2.38}$	$10^{5.48}$
CF₃CH₂OH	$10^{2.40}$	$10^{5.50}$
CH₃CO₂H	$10^{2.61}$	$10^{5.71}$
CH₃CH₂OH	$10^{3.31}$	$10^{6.41}$

[a] Obtained by multiplying $k^{4\text{-}OTs}/k^{2\text{-}AdOTs}$ by $10^{3.1}$, the inherent $k_c^{2\text{-}AdOTs}/k_c^{4\text{-}OTs}$ ratio.

tion that the k_A route is, indeed, the dominant pathway while the solvent unassisted pathway, k_c, plays only a

minor role in the solvolysis of **4-ONas**. The value of k_c(cyclobutyl)/k_c(2-adamantyl), the solvent invariant rate ratio,[4] was estimated by use of the rate data calculated by Schleyer[14] from steric and conformational considerations and by use of eq 1,[15] where

$$\log \frac{k_c 4\text{-OTs}}{k_c 2\text{-AdOTs}} \simeq \log \frac{k_{rel} 4\text{-OTs}}{k_{rel} 2\text{-AdOTs}} = \Delta(\text{steric strain})_{4-2} \quad (1)$$

it is noted that the steric strain term reflects the enhanced steric strain introduced into the cyclobutyl and 2-adamantyl systems by generation of trigonal center typical of a classical cation.

Experimental Section

A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector and 8 ft × 0.25 in. columns of 20% diethylene glycol succinate on Chromosorb W, AW-DMCS (45–60 mesh), and 20% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W (30–60 mesh) were used for analytical gc work.

Cyclobutyl β-naphthalenesulfonate (4-ONas) resulted when 2-naphthalenesulfonyl chloride (8.0 g, 0.35 mol) was mixed with cyclobutanol (2.16 g, 0.30 mol) and 40 ml of redistilled *sym*-collidine at 0°. After being allowed to stand 16 hr at 0°, the reaction mixture was acidified with cold, 10% aqueous HCl. The precipitated ester was separated on a Büchner funnel, washed three times with cold acid and three times with cold water, and air-dried to yield 7.3 g of crude ester. Recrystallization from 1:1 petroleum ether (bp 30–60°)–ether gave 4.6 g (58%) of white crystals, mp 75–76° (lit.[16] mp 75–76°).

Solvents.—Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride. Absolute ethanol was prepared according to the method of Fieser.[17] 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled just prior to use. Formic acid solvent was stored several days over boric anhydride, decanted, and distilled from fresh anhydride.

Cyclobutyl β-Naphthalenesulfonate Ethanolysis Products— Cyclobutyl β-naphthalenesulfonate (1.13 g, 5 mmol) was dissolved in sufficient absolute ethanol (containing 10 mmol of dry pyridine) to give 25 ml of solution. After 11 half-lives at 50°, the solution was diluted with 150 ml of water and continuously extracted with ether for 3 days. The ether extract was washed with dilute, aqueous HCl and cold water and dried (Na₂SO₄), and most of the solvent removed by distillation. Analysis by gc revealed, in addition to solvent, the presence of ethyl allylcarbinyl ether, ethyl cyclobutyl ether, and ethyl cyclopropylcarbinyl ether in the ratio 1:8.4:10.6, respectively.

Cyclobutyl β-Naphthalenesulfonate Acetolysis Products.— Cyclobutyl β-naphthalenesulfonate (1.13 g, 5 mmol) was dissolved in sufficient acetic acid solvent (containing 7.5 mmol of NaOAc) to give 25 ml of solution. After 11 half-lives at 50°, the solution was diluted with 150 ml of water and continuously extracted with ether for 2 days. The ether extract was neutralized with NaHCO₃, washed with water, and dried (Na₂SO₄)

(14) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964).

(15) Equation 1 is derived from the relative rate data of ref 14 as follows: $\log k_{rel}{}^x = \log k^x/k^{6\text{-}OTs} = (\text{steric strain})_x$; $\log k^y - \log k^{6\text{-}OTs} = (\text{steric strain})_y$; and, therefore, $\log k_{rel}{}^{4\text{-}OTs} - \log k_{rel}{}^{2\text{-}AdOTs} = \Delta(\text{steric strain})_{4\text{-}OTs - 2\text{-}AdOTs}$.

(16) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Amer. Chem. Soc.*, **83**, 4843 (1961).

(17) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Health, Boston, Mass., 1957, p 285.

and most of the solvent removed by distillation. Analysis by gc revealed, in addition to solvent, the presence of allylcarbinyl acetate, cyclobutyl acetate, and cyclopropylcarbinyl acetate in the ratio 1:11.0:13.0, respectively. A repeat of this product run where urea was used as the buffer in place of NaOAc gave the same analytical result.

Rate measurements were accomplished by usual techniques.[18] The titrating solutions were, for formolysis, 0.020 N sodium acetate in acetic acid and, for ethanolyses and trifluoroethanolyses, 0.020 N sodium methoxide in anhydrous methanol. The indicators used were bromphenol blue (in acetic acid), bromthymol blue (in water), and bromphenol blue (in 20% aqueous (EtOH), respectively.

(18) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

Treatment of Kinetic Data.—The rate constants, k, used in Figure 1 for the acetolysis and 2,2,2-trifluoroethanolysis were calculated according to the following scheme: $k = k_t/(F + F' + F'')$ which was derived from $k_t = Fk + F'k + F''k$ where F = fraction of ion pair yielding solvolysis products, F' = fraction of ion pair collapsing to allylcarbinyl β-naphthalenesulfonate, and F'' = fraction of ion pair collapsing to cyclopropylcarbinyl β-naphthalenesulfonate. It was assumed that the ratio of total anion collapse to solvent collapse is a constant in a given solvent independent of the detailed distribution of charge in the intermediate. For acetolysis, $k = 34.3 \times 10^{-7}$ sec^{-1} compared to $k_t = 24 \times 10^{-7}$ sec^{-1}. For 2,2,2-trifluoroethanolysis, $k = 16 \times 10^{-5}$ sec^{-1} compared to $k_t = 10 \times 10^{-5}$ sec^{-1}.

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Decomposition of p-Toluenesulfonylazoalkenes[1]

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p-Toluenesulfonylazostilbene and 2-p-toluenesulfonylazo-1,3-diphenylpropene have been synthesized and decomposed in benzene at 90° and in chloroform at 25°. The results obtained are consistent with a rearrangment of p-toluenesulfonylazoenes to the corresponding 2-p-toluenesulfonyldiazo compounds and successive protic decomposition. The formation of diphenylacetylene and 1,3-diphenylallene can be ascribed to an internal neutralization of vinyldiazonium ions.

Recently, two papers concerning the reaction of p-toluenesulfonylhydrazine with ketones bearing a leaving group on the adjacent carbon have appeared. The first paper[2] reports the formation of diphenylacetylene from benzoin acetate and benzoin benzoate p-toluenesulfonylhydrazones with alkali. The proposed mechanism, however, is at variance with experiments previously reported by us.[3,4] The second paper[5] concerns the reaction between p-toluenesulfonylhydrazine and α-X ketones via p-toluenesulfonylazoenes.

We wish to report here some experiments that confirm the peculiar reactivity of the S–N bond in p-toluenesulfonylazoalkenes. In aprotic solvents, treatment of α-acetoxydeoxybenzoin and α-acetoxy-1,3-diphenylpropane-2-one p-toluenesulfonylhydrazones with bases gives the corresponding p-toluenesulfonylazostilbene (I) and 2-p-toluenesulfonylazo-1,3-diphenylpropene (II).
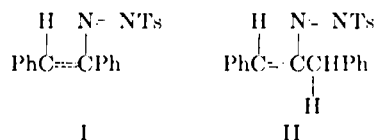
The mechanism of the formation of these compounds is consistent with 1:4 elimination of AcOH by basic treatment.[3,4] The p-toluenesulfonylazoenes obtained are yellow compounds which decompose on melting, and their structure has been assigned on the bases of analytical and spectroscopic data (Experimental Section).

The thermal decompositions of I and II in dry benzene at 90° resulted in the evolution of nitrogen and the disappearance of the yellow color of the solution. The

(1) This work was done with financial support of the Italian National Research Council (C.N.R.).

(2) T. Iwadare, I. Adachi, M. Hayashi, A. Matsunaga, and T. Kitai, *Tetrahedron Lett.*, No. 51, 4447 (1969).

(3) L. Caglioti, P. Grasselli, F. Morlacchi, and G. Rosini, *Chem. Ind. (London)*, 25 (1968).

(4) L. Caglioti and G. Rosini, *ibid.*, 1093 (1969).

(5) P. Wieland, *Helv. Chim. Acta*, **53**, 171 (1970).

mixtures obtained by evaporation of the solvent were separated by column chromatography on silica gel to give the compounds shown in eq 1 and 2.
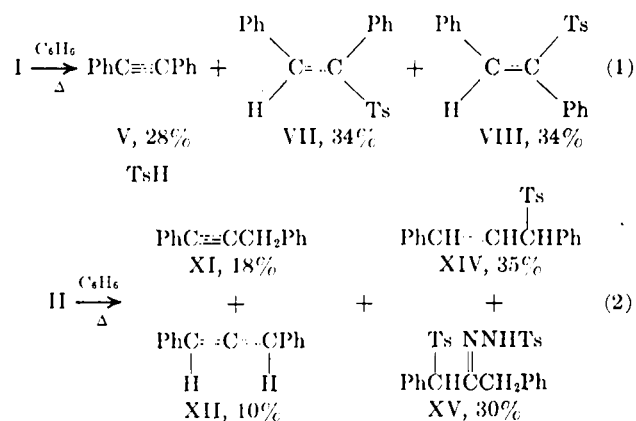
The same results were obtained if I or II were allowed to stand at room temperature for several hours in CHCl₃ solution. The yields of the products were substantially unchanged compared with those from the thermal decomposition in benzene.

In the case of I, the initial yellow color of the solution turned pink during the first hour of reaction, and then this color slowly disappeared while nitrogen was evolved. A pink compound (mp 95° dec from benzene–n-pentane) was obtained by removing the chloroform under reduced pressure, in the cold, when the pink color of the solution had become most intense. The analytical values and the physicochemical data suggest that this compound is 1-p-toluenesulfonyl-1,2-diphenyl-2-diazoethane (IV). The rearrangement of I to IV has been followed at 25° by scanning the visible spectrum between 350 and 700 mµ every 16 min. The disappearance of the band at 342 mµ of I is consistent with the formation of the band at 500 mµ of IV. The absorption curves for this transformation carried out at 25° in chloroform are shown in Figure 1.